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14. ABSTRACT We investigated photocatalytic decomposition of organic compounds on rutile TiO ₂ (110) single crystal surfaces in presence of near-UV light and O ₂ by two-photon photoemission spectroscopy. We found that the irradiation of water, methanol and ethanol induces deprotonation of the intact species to produce surface OH species. The surface OH is responsible for the intense wet electron resonance observed in two photon-photoemission spectra. Measurement of the wet electron resonance as a function of time indicated an initial rise of the signal due to the				
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Wet-electron Enhanced Surface Dissociative Electron Attachment Chemistry of Halocarbons - Final Report

ABSTRACT

We investigated photocatalytic decomposition of organic compounds on rutile TiO₂(110) single crystal surfaces in presence of near-UV light and O₂ by two-photon photoemission spectroscopy. We found that the irradiation of water, methanol and ethanol induces deprotonation of the intact species to produce surface OH species. The surface OH is responsible for the intense wet electron resonance observed in two photon-photoemission spectra. Measurement of the wet electron resonance as a function of time indicated an initial rise of the signal due to the production of the surface OH species to a saturation value, followed by periodic sharp changes in the signal of unknown origin. When the same experiment is performed in the presence of O₂ at 10⁻⁹ to 10⁻⁸ mbar pressure, the wet electron signal oscillates. Signal autocorrelation measurements provide evidence for an oscillatory photocatalytic process most likely involving the interaction of conduction band electrons with O₂ molecules and holes with the chemisorbed organic molecules. We believe that this is the first time that such oscillatory chemical reaction has been observed in a photocatalytic process, and it is likely to be a general phenomenon associated with the collocated oxidation and reduction processes on TiO₂ surfaces. Therefore it is relevant to the mechanism of photocatalytic decontamination with TiO₂ photocatalysis.

List of papers submitted or published that acknowledge ARO support during this reporting period. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

1. H. Petek and J. Zhao, "Ultrafast Interfacial Proton-coupled Electron Transfer," Chem. Rev. 110, 7082 (2010).
2. T. Minato, Y. Sainoo, Y. Kim, H. S. Kato, K.-I. Aika, M. Kawai, J. Zhao, H. Petek, T. Huang, W. He, B. Wang, Z. Wang, Y. Zhao, J. Yang, and J. G. Hou "The Electronic Structure and Spatial Distribution of Excess Charge Created by Oxygen Atom Vacancies on Titanium Dioxide Surfaces," Hyomen Kagaku (Journal of The Surface Science Society of Japan) 31, 474-479 (2010) (in Japanese).

Number of Papers published in peer-reviewed journals: 2.00

(b) Papers published in non-peer-reviewed journals or in conference proceedings (N/A for none)

H. Petek and J. Zhao, "Ultrafast spectroscopy of photocatalytic reactions on single crystal TiO₂ surfaces," Abstracts of the 2010 Annual Meeting of the Spectroscopical Society of Japan, Kyoto, Japan (2010)

Number of Papers published in non peer-reviewed journals: 1.00

(c) Presentations

1. Colloquium, Fritz Haber Institute; Berlin, Germany, Dec. 2, 2010. (invited)

Number of Presentations: 1.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts): 0

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts): 0

(d) Manuscripts

Number of Manuscripts: 0.00

Patents Submitted

Patents Awarded

Awards

Graduate Students

<u>NAME</u>	<u>PERCENT_SUPPORTED</u>
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FTE Equivalent:

Total Number:

Names of Post Doctorates

<u>NAME</u>	<u>PERCENT_SUPPORTED</u>
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Xuefeng Cui

0.95

FTE Equivalent:

0.95

Total Number: 1

Names of Faculty Supported

<u>NAME</u>	<u>PERCENT_SUPPORTED</u>
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FTE Equivalent:

Total Number:

Names of Under Graduate students supported

<u>NAME</u>	<u>PERCENT_SUPPORTED</u>
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FTE Equivalent:

Total Number:

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

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The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... 0.00

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Scientific Progress

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Wet-electron Enhanced Surface Dissociative Electron Attachment Chemistry of Halocarbons - Final Report

By time-resolved two-photon photoemission (2PP) spectroscopy and electronic structure theory, we have explored photocatalytic chemistry of small molecules on TiO₂(110) surfaces that are of interest to environmental remediation. In this report we will focus on some of the main results including: 1) the formation of wet electron states; 2) the theoretical structure of methanol chemisorption and wet electron states; and 3) oscillatory photocatalytic dynamics on TiO₂ surfaces. We describe each of these topics in turn.

The formation of wet electron states

In a previous MURI funded project we discovered the wet electron states for H₂O and CH₃OH overlayers on TiO₂ surfaces, where electrons excited from the TiO₂ substrate are trapped transiently in the protic solvent overlayer at an energy of about 2.3 eV above the Fermi level. We demonstrated that the primary site for stabilization of wet electrons is surface OH species, formed by the deprotonation or dissociation of the parent molecule. In addition, undissociated O-H or C-H species of the parent molecule help to stabilize the wet electron state.

In experiments supported by the present grant we have shown that the wet electron state does not exist on as deposited surfaces. If a monolayer of H₂O and CH₃OH are deposited on TiO₂ surface *with* concurrent irradiation with 400 nm light, the wet electron resonance appears as coverage approaches 1 ML (Fig. 1a). If the sample is moved then so that the laser excites a previously unirradiated spot, the wet electron state is initially absent from 2PP spectra, but it gradually rises in intensity for subsequent measurements as the irradiation dose is increased (Fig. 1b).

These observations indicate that the species responsible for the wet electron resonance is a product of a photocatalytic reaction, which once formed is relatively stable on the surface (but see further discussion below). In STM experiments of our collaborators (Bing Wang, University of Science and Technology, China), it was shown that 400 nm light dissociates both H₂O and CH₃OH molecules to produce the surface OH. So the rise of the wet electron state signal with irradiation is consistent with our assignment of the wet electron resonance to surface OH species. Such species can be generated by exothermic dissociation of the parent molecule at O atom vacancy defects, or by photocatalytic activity of the surface. The observation of the photocatalytic process is a new finding that will help to elucidate the process of organic

molecule mineralization on TiO_2 surfaces. The deprotonation dynamics are probably associated with proton-coupled electron dynamics,¹ which we have

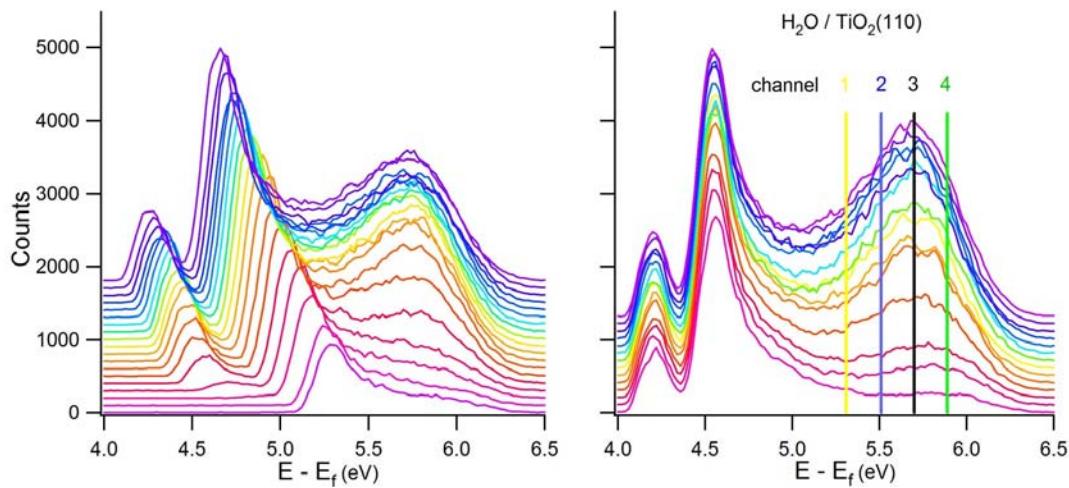


Figure 1. a) 2PP spectra as CH_3OH molecules are dosed onto TiO_2 surface observed in femtosecond time-resolved measurements.² If the laser spot is now translated to a yet unirradiated position, we can while simultaneously irradiating the surface. Wet electron peak is observed monitor continuously the rise to the wet electron state intensity with time. Figure 2 shows the 2PP intensity at 4 different energies, indicated in Fig. 1b, as a function of irradiation time. After about 300 s irradiation, the wet electron state laser irradiation occurs at a different spot. The vertical lines indicate the signal reaches a plateau. The intensity, however, does not rise smoothly, and is punctuated by sharp negative bursts of unknown origin. Now, we can only speculate the origin of these bursts. Near-UV excitation of TiO_2 surface excites electron hole pairs across the 3.0 eV band gap. Because holes have a large overpotential for oxidation of H_2O , it is likely that the deprotonation to form surface OH is a hole-driven process. How the hole attack occurs, however, is unclear because the hole acceptor states of H_2O are too deep for this to be an exothermic process. We are currently studying the nature of the acceptor states by density functional theory (DFT). Regardless of how it happens, the consumption of one type of carrier (holes) leaves a surfeit of the other (electrons). We believe that the occasional negative bursts are associated with the buildup of electrons and the associated Coulombic interactions this introduces into the TiO_2 surface. Further research is required to obtain more clear understanding. We will return to a discussion of carrier dependent interactions shortly.

Theoretical structure of CH₃OH chemisorption and wet electron states

In order to understand the relative stability of the molecular vs. deprotonated chemisorption of H₂O and CH₃OH, we performed extensive DFT calculations of CH₃OH on rutile TiO₂ surface. Similar calculations have been performed for H₂O on TiO₂ with controversial outcome. What is clear is that for H₂O the two forms are nearly isoenergetic and their relative stability depends on the level of theory used in the calculation.

We have examined 11 different structures of CH₃OH on TiO₂ for 1 monolayer (ML) coverage, where one CH₃OH molecule is chemisorbed per one Ti surface site. We demonstrated that it is necessary to perform such calculations to at least 11 TiO₂ tetrahedron slabs, in order to obtain converged adsorption energies.³ Some of the theoretical discrepancies for H₂O chemisorption can be

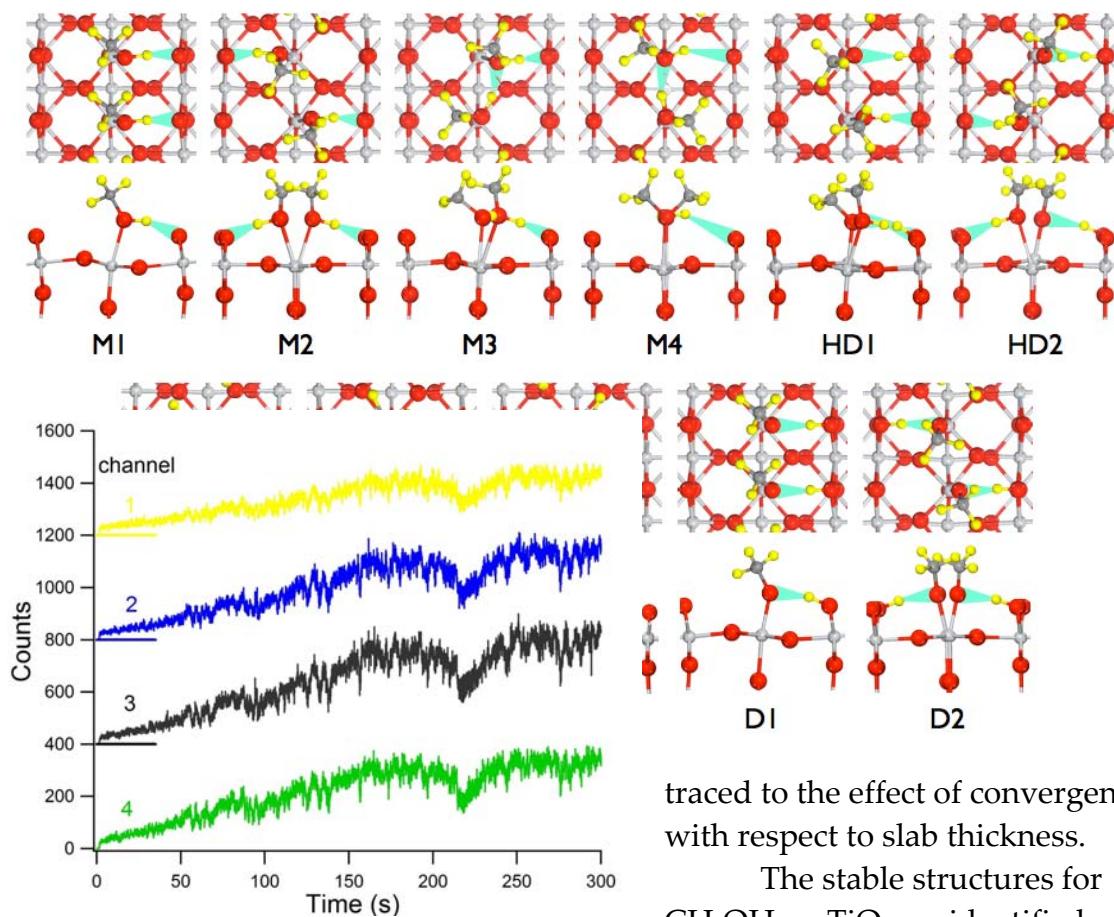


Figure 3. The calculated top and side views of chemisorption structures for two methanol molecules per (2×1) TiO₂(110) surface unit cell. Light grey, red, dark gray, and yellow spheres indicate respectively Ti, O, C, and H atoms. Blue rays connect H and O atoms participating in hydrogen bonds. M, HD,

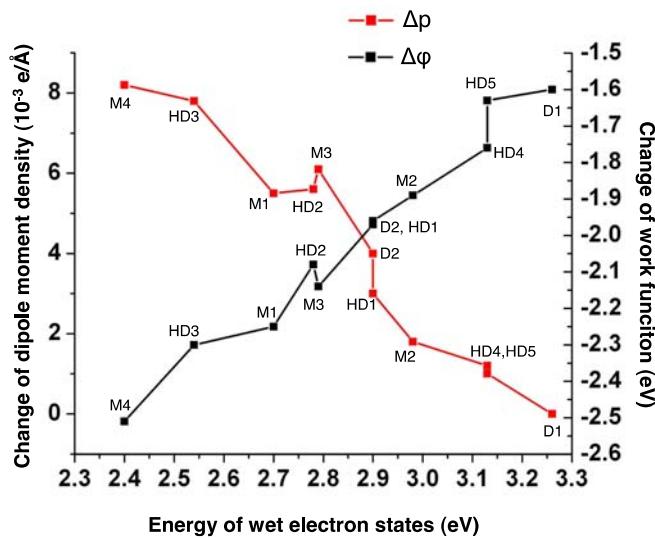
Figure 2. The 2PP intensity as CH₃OH/TiO₂ surface is irradiated with 3.1 eV light vs. irradiation time. Measurements are performed at the energies

traced to the effect of convergence with respect to slab thickness.

The stable structures for CH₃OH on TiO₂ we identified are

shown in Fig. 3. The calculation was performed for two methanol molecules for a double surface unit cell to allow for different molecule-molecule and molecule-surface interactions. The most stable methanol structures involve molecular chemisorption with one molecule making intermolecular hydrogen bond and the other, a molecule-surface hydrogen bond. The next most stable structures are singly deprotonated, and the least stable ones are the doubly deprotonated structures. The reason why intermolecular and molecule-surface hydrogen bonds are favored in alternating molecules appears to be steric hindrance. The alternation of hydrogen bonds helps to reduce steric hindrance with respect to having just one type of bond. In addition to hydrogen bonding and steric hindrance, it appears that surface stress also makes an important contribution to overall chemisorption energy. It is likely that similar interactions are important for the chemisorption of other molecules on TiO_2 surfaces, but the details will depend on specific structure-dependent factors.

In addition to the chemisorption structure, we also investigated the wet electron states on TiO_2 surfaces. Figure 4 shows the correlation of wet electron state energy with the surface dipole moment. The chemisorption structures that have the largest dipole moment also have the lowest energy wet electron states. This is quite reasonable because the largest dipole moment is associated with the most acidic hydrogen atoms of the overlayer. The more the electron charge in the ground state is withdrawn to the substrate, the better are the surface H atoms as wet electron state acceptors. The range of wet electron state energies in Fig. 4 is consistent with the large width of the wet electron resonance for CH_3OH on



TiO_2 surface. The correlation of the wet electron stabilization with acidic H atom density suggests that in solution phase systems, the role of wet electrons is likely to be more important for low pH conditions.

Figure 4. The correlation between the dipole moment density, the work function change with respect to the clean TiO_2 surface, and the wet electron state energy with respect to Fermi level for different CH_3OH chemisorption structures. The structures are

Oscillatory photocatalytic dynamics on TiO_2 surfaces

So far we have described the properties of single species (H_2O or CH_3OH) on TiO_2 surfaces under ultrahigh vacuum conditions. There is evidence from XPS spectroscopy that even at much higher background pressures at room temperature, TiO_2 surfaces are covered by approximately 1 ML of water. Under ambient conditions that would be pertinent for chemical remediation, O_2 is likely to be an important reactant in decomposition of organic molecules. Therefore, we investigated the effect of O_2 on TiO_2 photocatalysis with H_2O and CH_3OH overlayers.

For a clean TiO_2 surface at 90 K O_2 molecules do not adsorb on stoichiometric TiO_2 surfaces; they only react at and heal O atom vacancies. Therefore, it is not surprising that exposing H_2O or CH_3OH covered TiO_2 surface to O_2 atmosphere does not change the general shape of 2PP spectra. The spectra, however, take on a rather noisy appearance with the noise depending on the O_2 background pressure. We therefore measured the time course of the wet electron peak intensity, as in Fig. 2, at several energies with different background pressures of O_2 . Figure 5a shows the time course of 2PP intensity at the wet electron energy for a background pressure of 3×10^{-8} mbar of O_2 . The 2PP signal in Fig. 5a is clearly fluctuating with time in a manner that is correlated for different observation energies. The fluctuation amplitude increases with the background O_2 pressure. Such behavior is characteristic of oscillating chemical reactions, which have been observed in catalytic processes and are thought to be responsible for circadian rhythms in biological clocks.

In order to confirm this interpretation, we performed an autocorrelation analysis of the signal in Fig. 5a, which is displayed in Fig. 5b. The autocorrelation function shows a damped oscillating behavior that is consistent with the interpretation of an oscillating chemical system that is far from thermodynamic equilibrium. Although we are far from being able to provide a model for the observed behavior, we speculate that some of the ingredients for the oscillating photocatalytic activity include: 1) optical generation of electrons and holes, which provide the thermodynamic driving force; 2) the spatially separated chemical reactivity of electrons and holes with respect to reactants; 3)

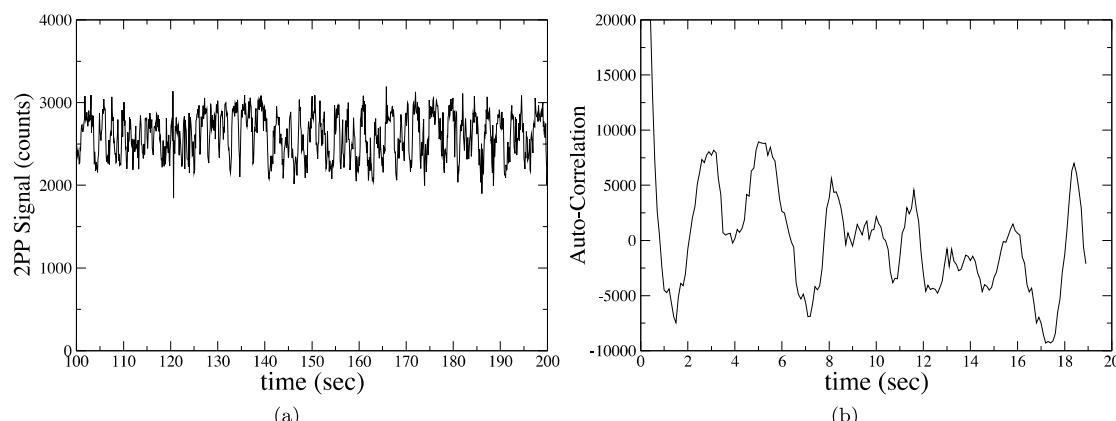


Figure 5. a) The oscillating wet electron state intensity in presence of gas phase O_2 at 3×10^{-8} mbar pressure; and b) the autocorrelation of the periodic fluctuation

transport of O₂ molecules to and reaction at TiO₂ surface; 4) oxidation of CH₃OH by holes; and 5) reduction of O₂ to O₂⁻ by electrons. There is evidence that oxidation and reduction processes on TiO₂ occur at spatially different locations. With only CH₃OH on the surface, we can only drive oxidation process, leading to accumulation of excess electrons, which may be responsible for the bursts in Fig. 2. With both red-ox processes occurring in the presence of O₂, we see the oscillations. The separate processes enumerated above could be described by a set of nonlinear differential equations, which in certain regimes would lead to nonlinear, chaotic, and oscillating solutions. At this stage this is our hypothesis, and we plan to do further research to establish a kinetic model to describe these oscillating chemical processes. Being able to describe photocatalytic decomposition of organic molecules in presence of O₂ and light would represent a major step in understanding the photocatalytic properties of TiO₂.

Other accomplishments

Besides the topics described above, we have also performed the research described briefly hereafter. More extensive descriptions have been provided in previous reports:

1) Characterization of the electronic properties of O atom vacancies on TiO₂. By low temperature STM and electronic structure theory we characterized the distribution of charge at TiO₂ surface following removal of O atoms. Such defects are present at few-percent level on any TiO₂ surface prepared by UHV surface science methods, and they represent the most reactive sites for thermal chemistry. We have shown that the charge density is distributed over multiple Ti sites, and therefore it can attract electrophilic and repel electrophobic reactants with respect to O atom vacancy defects.⁴

2) The GW calculation of the electronic band structure and exciton properties of anatase and rutile TiO₂. Despite being a paradigm for photocatalytic chemistry, the electronic structure of TiO₂ had not been investigated by high-level electronic structure theory. We have calculated the optical spectrum of TiO₂ by the GW method, which is known to give accurate results for optical properties of semiconductors, and metal oxides. Our calculations are a starting point for understanding how the electronic structure of TiO₂ determines the properties of electrons, holes and excitons that are generated by optical excitation.⁵

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(2) Li, B.; Zhao, J.; Onda, K.; Jordan, K. D.; Yang, J.; Petek, H.: Ultrafast interfacial proton-coupled electron transfer. *Science* **2006**, *311*, 1436-1440.

(3) Zhao, J.; Yang, J.; Petek, H.: Theoretical study of the molecular and electronic structure of methanol on a TiO₂(110) surface. *Phys. Rev. B* **2009**, *80*, 235416-11.

(4) Minato, T.; Sainoo, Y.; Kim, Y.; Kato, H. S.; Aika, K.-i.; Kawai, M.; Zhao, J.; Petek, H.; Huang, T.; He, W.; Wang, B.; Wang, Z.; Zhao, Y.; Yang, J.; Hou, J. G.: The electronic structure of oxygen atom vacancy and hydroxyl impurity defects on titanium dioxide (110) surface. *J. Chem. Phys.* **2009**, *130*, 124502-11.

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